



Fundamentals of CO detection examined

Two-photon laser-induced fluorescence (TPLIF) and Raman scattering are the two prevailing methods for *in situ*, point-specific monitoring of CO within combustion gases. Between them, TPLIF promises the greater sensitivity. With the experimental work of Michael Di Rosa, Roger Farrow, and Paul Schrader, the method is gaining accuracy for the cross sections that govern the conversion of signal to concentration.

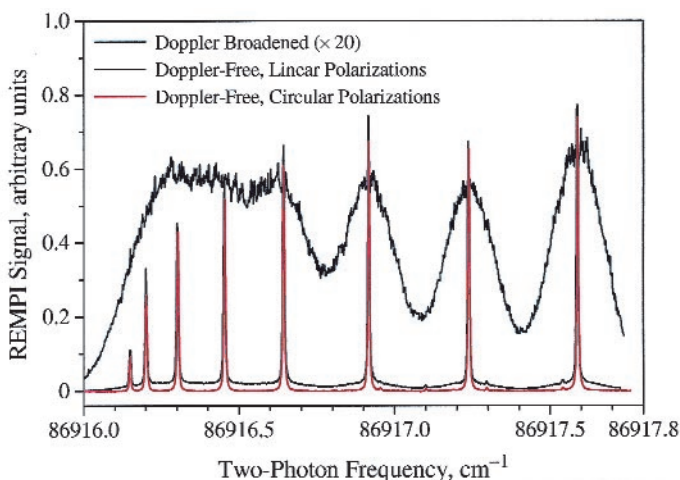


Figure 1. Improvement in resolution of excitation spectra, progressing from Doppler-broadened, to Doppler-free with linearly polarized light, to Doppler-free with circularly polarized light. The three REMPI spectra were recorded for 1 torr (0.1 kPa) CO, 293 K, and a total light energy of 0.5 μJ /pulse.

The components of CO TPLIF reside within an overall process of resonance-enhanced multiphoton ionization (REMPI) that ultimately generates CO^+ ions (and electrons). In the resonance step, a laser pulse at 230 nm promotes two-photon absorption transitions to an upper state that subsequently fluoresces at wavelengths from the blue to green, forming the LIF signal. The laser pulse produces CO^+ ions by this same upper state absorbing 230 nm light. If efficiently collected by a voltage-biased probe, the REMPI-produced ions can generate a signal even more sensitive to CO than is TPLIF. Both methods of detection, TPLIF and REMPI, then draw on the upper state and depend on the rate at which it is photoionized, though in opposite ways. An increased photoionization rate, for example, augments REMPI signals at the expense of TPLIF.

Michael and coworkers are measuring the photoionization rate through a novel application of high-

resolution spectroscopy that begins with isolating the individual transitions composing the resonance, or excitation, step to the upper state. The REMPI spectra of Figure 1 show the improved resolution achieved when progressing from excitation schemes of single-pass (producing the blue curve), Doppler-free with linear polarization (black), and Doppler-free with circular polarization (red). This last technique renders a reference spectrum of transitions projecting as narrow "spikes" from a flat baseline.

The reference-excitation process is then exposed to an intense laser pulse tuned near 230 nm that greatly enhances the photoionization rate. In response, as seen in Figure 2, the transitions shift and broaden. The shift occurs through an a.c. Stark effect, and the increased broadening is directly related to the increased photoionization rate, which acts to reduce the lifetime of the upper state. Cross sections for Stark shift and photoionization derive from the observed linear growth of the shift and width with increasing intensity of the photoionization pulse.

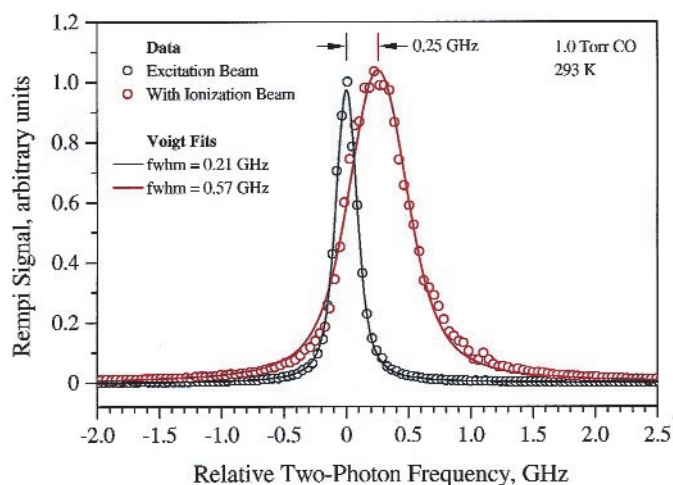



Figure 2. Response of Q(12) of CO $\text{B} \leftarrow \text{X}(0,0)$ to non-resonant photoionization at 229.285 nm and an average intensity of 220 MW/cm^2 . Conditions were 1 torr (0.1 kPa) CO, 293 K, and an excitation-beam intensity of 15 MW/cm^2 .

Other equally important components of TPLIF and REMPI are also being studied to extract their characteristic cross sections, many of which are only vaguely known. Present and planned studies include measurements of cross sections for two-photon excitation, collisional broadening and shift, and electronic quenching. 



Frank Behrendt (left, University of Heidelberg) was recently hosted by Bob Gallagher for an extended visit. Frank used his time at the CRF to complete research he had initiated several years ago in the area of catalytic combustion.

27th International Combustion Symposium

CRF Staff played an active role in the 27th International Combustion Symposium at the University of Colorado, August 2-7, 1998. Over 750 technical papers from 32 countries were submitted to the Symposium; of the 377 accepted papers, 19 were coauthored by CRF researchers. To help organize the Symposium, Jim Miller cochaired the Colloquia on Reaction Kinetics of Combustion, including Pollutant Formation and Control, and Don Hardesty served as cochair with Brian Haynes (University of Sydney) of the Technical Program. Nine technical sessions were cochaired by CRF researchers.

A major step in planning and developing the technical program was facilitated by use of a new web-based tool developed by Ken Buch (Limit Point Services). Ken's Web-Assisted Symposium Program linked the Symposium websites of the University of Colorado and the Combustion Institute, as well as the Institute's database of reviewers, to the program and colloquia chairs, who used the tool to select reviewers, process data, and assemble the program.

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Thermodynamic database online

A new web-based database of thermodynamic and kinetic information is now available at www.ca.sandia.gov/crf/research/Applied/ThermoKinData/. The site provides two kinds of information: First, thermodynamic data in the form of polynomial fits in Chemkin format for about 400 gas-phase species. Most of the species contain silicon, carbon, and/or boron. Second, a limited number of kinetic mechanisms developed for the prediction of various aspects of high-temperature materials synthesis processes (primarily chemical vapor deposition based). The bulk of the thermodynamic data were obtained from BAC-MP4 calculations performed by Carl Melius, Mark Allendorf, and Pauline Ho. Data can be downloaded to a user's computer in Mac, PC, or Unix formats.



Mike Westley (center), a student of Professor Paul Houston's at Cornell University, joined Thomas Lorenz (left) and Dave Chandler (right) to study collisional energy transfer using a newly developed crossed molecular beam/ion-imaging apparatus. Mike measure the differential cross section for the rotational energy transfer between NO molecules and either He atoms or D₂ molecules.

Diesel Combustion Collaboratory demo

The DCC project demonstrated recent progress and capabilities as a participant in the DOE2000 booth on the exhibit floor of the SC98 Conference on High Performance Networking and Computing, held November 7-13 in Orlando Florida (www.supercomp.org/sc98/). The booth included a display engine with a cut-away view of the workings of a diesel engine combustion chamber provided courtesy of Cummins Engine Company. DCC (www-collab.ca.sandia.gov) is a pilot project involving researchers at the Sandia, Los Alamos, and Lawrence Berkeley National Laboratories, the University of Wisconsin, Caterpillar, Cummins, and Detroit Diesel. The project goal is to assemble and implement collaboratory technology to facilitate DOE's Heavy Duty Diesel Combustion CRADA.

¹CH₂ measured in flames by cavity ring-down spectroscopy

Although an important combustion intermediate, ¹CH₂ has remained difficult to detect in flames. Highly reactive, ¹CH₂ cannot be detected via trapping or transfer-line techniques. Methylene is often detected by molecular beam mass spectrometry; however, this method cannot distinguish between the excited singlet state and the ground triplet state since their ionization potentials differ by only ~0.3 eV. Laser-induced fluorescence (LIF) has been used to detect ¹CH₂ in a low-pressure flame, but has proven difficult for routine detection due to rapid fluorescence quenching. Andrew McIlroy and Ed Bochenski have used cavity ring-down laser absorption spectroscopy (CRLAS) to detect ¹CH₂ in low-pressure methane flames with good signal-to-noise ratios (S/N).

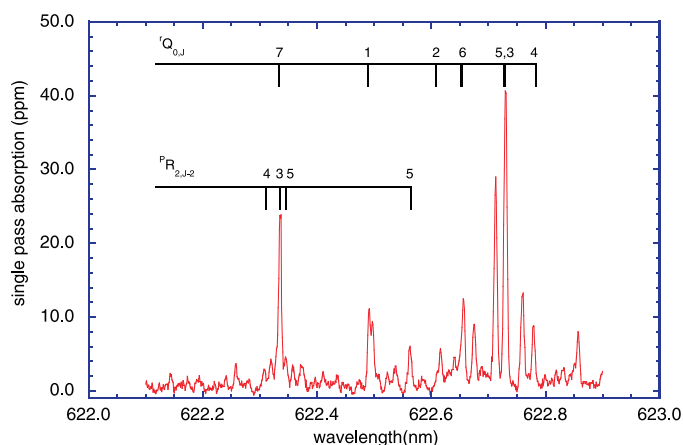


Figure 1. Sample ¹CH₂ spectrum fragment of the (0,13,0)-(0,0,0) band at the concentration maximum in a 31-torr, $\phi=1.2$ CH₄/O₂/Ar flame. Unassigned lines are also likely singlet methylene transitions.

Singlet methylene is an ideal candidate for detection by CRLAS. Accessible transitions lie in the visible where mirrors can easily be produced with the high reflectivity required. Since CRLAS is absorption based, it is immune to quenching effects that make ¹CH₂ LIF so difficult. The ¹CH₂ transitions near 620 nm are particularly convenient since the same mirror set can be used to detect HCO near 614 nm. Figure 1 shows a sample ¹CH₂ spectrum near the concentration peak in a CH₄/O₂/Ar flame with a stoichiometry of 1.2. The S/N of the largest peak is approximately 30. However, this is a blended line that cannot easily be used for quantitative concentration measurements. For this purpose, two lines that are apparently more isolated, ¹Q_{0,4} and ¹Q_{0,7}, are used.

The relative concentration profiles of ¹CH₂ in a series of rich methane flames at 31 torr (4.13 kPa) with stoichiometries of 1.0, 1.2, 1.4, and 1.6 have been

measured. The temperature-corrected ¹CH₂ data from the ¹Q_{0,4} and ¹Q_{0,7} rotational lines agree well (see Figure 2), suggesting that the two lines are correctly assigned and are free from contamination by other transitions. In order to compare the relative profiles to model predictions, they have applied a single scaling factor to the data to give the best overall agreement between the data and GRI 2.11 and Prada-Miller models for the 1.0 and 1.2 flames.

Figure 2 shows comparisons of these scaled data to both models. The widths and peak positions of the concentration profiles agree well for the 1.0 and 1.2 flames. For the 1.4 flame, the experimental peak is slightly closer to the burner than the models predict, but the width is correct. The 1.6 flame shows good agreement in peak position and width. Both models predict the peak concentration to rise from stoichiometries of 1.0 to 1.4, but to fall again at 1.6. The data quantitatively reproduce this trend from 1.0 to 1.4, but show a continuing increase in [¹CH₂] at $\phi=1.6$. This is the most significant discrepancy between the experiment and models.

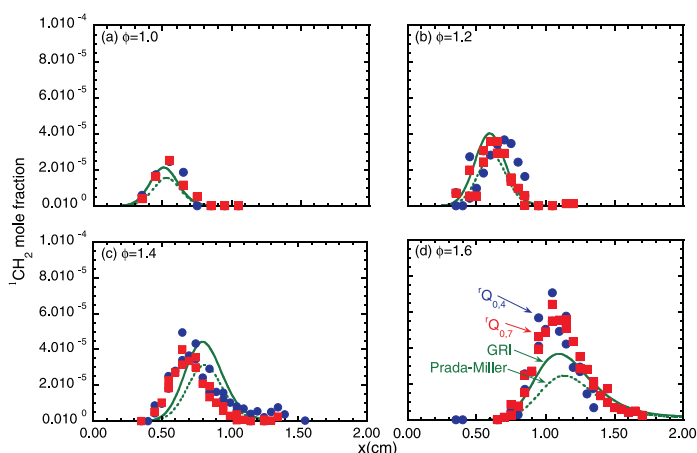



Figure 2. Singlet methylene concentration profiles in four 31-torr (4.13 kPa) methane flames with stoichiometries of (a) 1.0, (b) 1.2, (c) 1.4, and (d) 1.6 as a function of height above burner. The symbols are the temperature-corrected experimental points scaled to give the best overall agreement with the models at stoichiometries of 1.0 and 1.2. The circles and squares are data from the ¹Q_{0,4} and ¹Q_{0,7} transitions, respectively. Lines represent model predictions based on the GRI 2.11 mechanism (solid line) and the Prada-Miller mechanism (dashed line).

Experiments are currently underway to measure the absorption cross sections for the transitions detected. With these additional data, CRLAS will be a useful diagnostic for measuring absolute ¹CH₂ concentrations in combustion systems and other applications. 

Advisory Board; Adams and Bastress Awards

Photos of the Advisory Board, which met in November, are displayed on the CRF website, www.ca.sandia.gov/crf/WhatsHot/WhatsHot.html. At the same location, press Previous Issues to go to the November What's HOT, which featured Carl Melius and Dennis Siebers, recipients of the annual Adams and Bastress Awards, respectively.

Mixing process revealed in a modern SI engine

During the gas exchange process in a spark ignition engine, combustion products from the previous cycle remain in the cylinder while fuel and air for the next cycle are drawn in. The quantity of each gas and the state of mixing between them affect the quality of the combustion. Peter Hinze and Paul Miles have investigated mixing between fresh charge (premixed C_3H_8 and air) and combustion residuals in a modern engine with spontaneous Raman scattering. These results provide a better understanding of the state of the charge, important information for engine modeling and design.

Figure 1 shows a schematic of the diagnostic apparatus and the engine, a single-cylinder version of a modern 4-valve, pent-roof head geometry. The beam from a 532 nm pulsed laser enters the engine through a window in the head, passing within a few millimeters of the spark plug. The light scattered from a 15-mm long portion of this beam is imaged through a quartz window in the piston onto the slit of an imaging spectrograph, which spectrally disperses the image. This results in multiple images on the CCD detector, each corresponding to a different molecular species; the current system can simultaneously measure all major species of combustion: CO_2 , CO , O_2 , N_2 , fuel, and H_2O . The image for each species contains

spatial concentration information for the imaged portion of the beam, permitting determination of the mixing-length scales along the measurement volume.

Both ensemble-averaged and cycle-resolved images have been acquired. The ensemble-averaged images measure the mean charge composition, while the cycle-resolved images characterize the statistical nature of the in-cylinder mixing and reveal spatial details that are obscured by averaged measurements. Figure 2 shows histograms of the residual gas mole fraction near the spark plug for 500 cycles of data at five different crank angles during the cycle. Data taken during the intake stroke (-285 and -180 CAD), exhibit an extremely large dispersion in the residual mole fraction measured. As the compression stroke progresses (e.g., -90 and -60 CAD), the spread of the distribution narrows until time of spark (-15 CAD), where the observed coefficient of variation of the fluctuations is approximately 3%. Mixing-scale measurements indicate that the charge is not completely mixed at time of spark, suggesting that inhomogeneities in composition may contribute to cycle-to-cycle combustion variations.

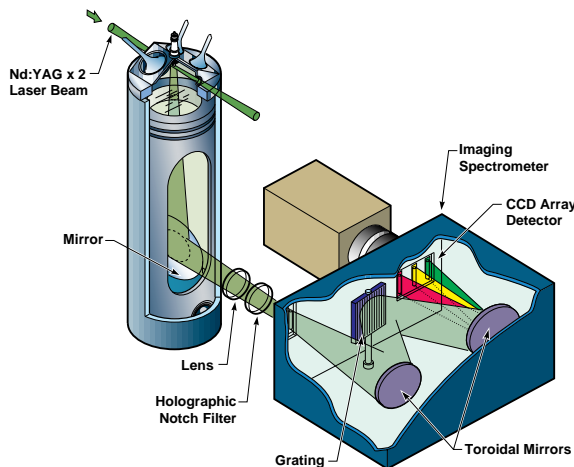


Figure 1. Schematic of the spontaneous Raman scattering experimental apparatus.

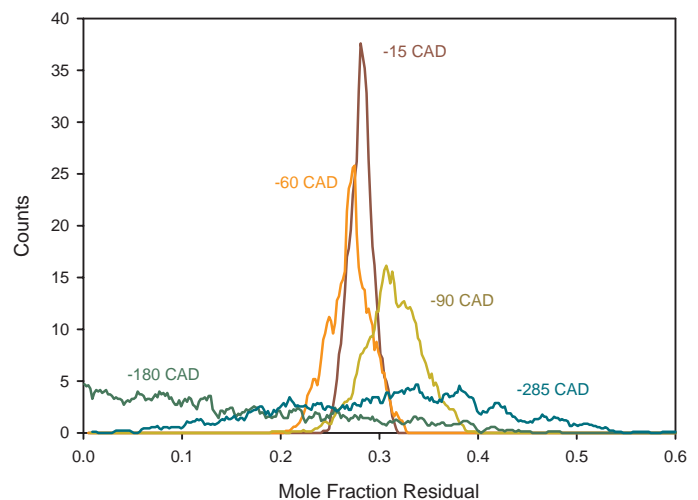


Figure 2. Histograms of measured residual mole fraction for five crank angles during the cycle. The bottom-center before-compression position of the piston is designated as -180 CAD.

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